Condensation and evaporation of mutually repelling particles: Steady states and limit cycles

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(Received 28 April 2004; revised manuscript received 11 August 2004; published 30 December 2004)

We study condensation and evaporation of particles which repel each other. The system evolves through a computer simulation using a simple set of rules on a square lattice. Different results are obtained for a mobile and an immobile surface layer. A two point limit cycle is observed for high temperature and pressure in both cases. Here the coverage oscillates between a high and a low value without ever reaching a steady state. The results for the immobile case depend in addition on the initial coverage.

DOI: 10.1103/PhysRevE.70.061609 PACS number(s): 68.43.De, 07.05.Tp, 05.70.Np, 68.43.Mn

I. INTRODUCTION

The dynamics of evaporating drops and its relation to the geometry of the drops is a well studied problem [1,2]. Different characteristics of aqueous interfaces with different hydrophobicities using molecular dynamics have also been studied [3,4]. Recently computer simulations on cellular automata type models [5–7] have been suggested which simulate the development of a surface layer under different physical conditions. A randomly occupied square lattice is taken and particles are allowed to stick/adsorb at vacant sites or evaporate/desorb from occupied sites according to a prescribed set of rules. Appropriate probabilities for the adsorption and desorption are set according to prescribed temperature and pressure conditions. We can also introduce an effective interaction between the particles by making the probabilities a function of the surroundings of a site, e.g., the number of nearest neighbors.

In the present paper we introduce an effective repulsive interaction between particles, by allowing the adsorption probability at an empty site to decrease with the number of occupied nearest neighbours. The desorption probability is a function of temperature of the substrate only. The results are very interesting. We start with a randomly occupied square lattice and study the evolution of a mobile layer by analytical and numerical methods and an immobile layer by computer simulation. In both cases we find a steady-state final coverage under some conditions. A two-point limit cycle showing oscillations in the coverage is observed, when the pressure is low while a temperature difference is maintained between the substrate (where adsorption takes place) and the surrounding vapor phase.

Standard literature on the study of surfaces involves sophisticated techniques, such as density functional theory and incorporate detailed interparticle interactions. A lot of work has been done recently along these lines [8–11]. The motivation of the present work is to show that a very simple and general model can show interesting behavior such as oscillations and hysteresis effects [5], simply by incorporating a repulsive or attractive interaction between adsorbate particles. Oscillatory adsorption has been observed in experiments by Patrylak *et al.* [12], so our results seem realistic. Minko *et al.* [13] report oscillation in polymer adsorption and calculations by Shioi *et al.* [14] show oscillations in adsorption and desorption in situations far from thermodynamic equilibrium. Adsorption with repulsive interaction between particles has been reported [11]. Another possibility of having a repulsive interaction is with similarly charged particles condensing on an oppositely charged substrate. In the next section we describe the model in detail. The results are presented in the third section and discussion and conclusions in the last.

II. MODEL

The process of adsorption/desorption is described traditionally by two different sets of models—one for a mobile adsorption layer and one for an immobile layer [15,16]. The probabilities for adsorption and desorption on a two-dimensional monolayer are specified according to the physics behind the model. These are functions of the temperature of the substrate, pressure, and the existing coverage. At equilibrium, the adsorption and desorption probabilities are set equal and the resulting equation is solved to get the equilibrium coverage at that temperature and pressure.

The simplest mobile layer model is a two-dimensional ideal gas, and the improved versions include interaction between particles, similar to a two-dimensional van der Waals gas. The so-called immobile layer models introduce an adsorption probability, depending on how long a molecule in the vapor above the surface is in contact with a surface site. The simplest "immobile model" is the Langmuir equation derived as follows.

For vapor adsorption the particle flux, i.e., the number of particles deposited per unit time per unit surface area (N) is given by

$$N = \frac{P}{\sqrt{2\pi mkT}} = \frac{P\lambda}{h}, \tag{1}$$

where P is the pressure,

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$$\lambda = \sqrt{h^2/(2\pi mkT)}$$

is de Broglie length, h is Planck's constant, m is the mass of a particle, k is Boltzmann's constant, T is the absolute temperature.

The probability of adsorption per unit time is obtained by dividing N by the total number of sites available for adsorption, and the same may be done for the desorption probability. The flux of desorption from a saturated surface may be approximated by [17]

$$d = \frac{kT}{h\lambda^2}\exp(-E_e/kT), \tag{2}$$

where E_e is activation energy for desorption. The prefactor to the exponential term is a function of the attempt frequency, i.e., the frequency of vibration of a particle in a local potential minimum (adsorption site) on the surface, hence it can be written in terms of the de Broglie wavelength λ. Denoting the fraction of occupied sites (i.e., the coverage) by c, adsorption probability is set equal to desorption probability, giving the equilibrium condition

$$\frac{P\lambda^3}{kT}(1-c) = \exp(-E_e/kT)c, \tag{3}$$

and we have the simple Langmuir equation

$$Pb = \frac{c}{1-c}, \tag{4}$$

where

$$b = \frac{\lambda^3}{kT}\exp(E_e/kT).$$

In this approximation it is assumed that desorption energy is the same for all configurations.

In the present work we introduce a repulsive interaction between particles, as follows—adsorbing particles are less likely to stick at sites surrounded by more neighbors. This mimics a situation where the adsorbing particle has to overcome the potential barrier due to the repelling neighbors to reach a vacant site on the substrate. We assume that the substrate attracts the adsorbing particle.

We define a probability for adsorption on a vacant site f_c determined by the pressure P as

$$f_c = P/P_s = P^*, \tag{5}$$

where P_s is a saturation pressure and $0 < f_c < 1$. P^* is the reduced pressure defined by P/P_s. The adsorption probability at a vacant site with n occupied neighbors is proportional to f_c^n. We have

$$\begin{aligned}\Pi_{ads} &= (1-c)^5 + 4(1-c)^4 c f_c + 6(1-c)^3 c^2 {f_c}^2 \\ &\quad + 4(1-c)^2 c^3 {f_c}^3 + (1-c)c^4 {f_c}^4 \\ &= (1-c)(cf_c + 1 - c)^4.\end{aligned} \tag{6}$$

The successive terms in the central expression above represent the probability of a vacant site having, respectively, 4, 3, 2, 1 and 0 vacant near neighbor sites.

The desorption probability is assumed to be a function of T, the temperature of the substrate, and, of course, c, but is assumed independent of the occupancy of neighboring sites. The temperature of the substrate is different from the temperature of the gas phase, which is determined by the pressure and the constant volume of the system. So our system is an "open" system with a constant inflow of energy, to maintain the steady temperature difference.

$$\Pi_{desorb} = c(kT/P_s\lambda^3)\exp(-E_e/kT). \tag{7}$$

P_s is temperature dependent, and this must be taken into account. But we can approximate it by the simple relation that follows from the equilibrium relation on the surface of the fluid:

$$P_s = \frac{kT}{\lambda^3}\exp(-E_{vap}/kT), \tag{8}$$

where E_{vap} is the enthalpy of vaporization of a fluid that supports vapor.

In this formulation the simplest adsorption desorption equilibrium condition is obtained by equating Π_{ads} and Π_{desorb},

$$(1-c)(cf_c + 1 - c)^4 = \frac{kT}{P_s\lambda^3}\exp(-E_e/kT)c = \exp(-\Delta E/kT)c, \tag{9}$$

where $\Delta E = E_e - E_{vap}$. Here too the adsorption probability f_c is given by Eq. (5) and the desorption probability is

$$f_e = \exp(-\Delta E/kT). \tag{10}$$

The adsorption probability is a function of the reduced pressure P^* only. That means that the molecules desorb from the surface with a probability 1 when $E_e = E_{vap}$, i.e., when the energy of desorption from the surface E_e equals the energy of desorption E_{vap} from the surface of a liquid that supports the vapor.

So, we can rewrite the probability for an adsorbed particle desorbing (Π_{desorb}) as

$$\Pi_{desorb} = cf_e = c\exp(-1/T^*), \tag{11}$$

where $T^* = kT/\Delta E$.

Our model is complementary to the Fowler-Guggenheim model [15,16], where the adsorption probability is dependent only on pressure, but the desorption probability decreases with the number of occupied near neighbors. The neighbors are assumed to attract the particle and create a barrier to desorption. This type of interaction was incorporated in Dutta *et al.* [5].

Now we study the behavior of this system for different values of the temperature and pressure parameters. We look at the two different situations where the surface layer is either mobile or immobile.

A. Mobile surface layer

Let us suppose that the energy barrier for motion of the adsorbed particles along the surface is very low so a continu-

ous rearrangement is going on. In this case the distribution of particles always becomes random and the probabilities in Eq. (6) are always valid. So one can equate the adsorption and desorption probabilities in the steady state and solve for the coverage c. We confine ourselves to ranges of T^* and P^*, which give adsorption and desorption probabilities in the range 0–1. The results are shown in the next section. We may also see how the coverage evolves using the following iterative procedure:

$$c_f = c_i + \Pi_{ads} - \Pi_{desorb} \tag{12}$$

and

$$c_i = c_f, \tag{13}$$

where c_i is the initial coverage and c_f the final. If there is a steady-state solution the final coverage c_f converges to a steady value. We find, however, that for some combinations of the pressure and temperature parameters, the coverage converges to a stable limit cycle, oscillating between two positive and realistic values. The solution for c in Eq. (9) now becomes an unstable fixed point. This is very interesting and reminiscent of the discovery of oscillatory behavior in real chemical systems [18–20]. Such oscillations are observed in far from equilibrium situations, in open systems, where a feedback loop is present, as constituted by Eq. (12) and (13).

The results obtained here can be verified from a computer simulation on a finite system. This was done as follows. We assume that a gas occupies the space above a square lattice. The gas molecules can adsorb or desorb from sites on this lattice with a probability that is determined by its pressure and the configuration of the nearest neighbor sites at a given point. The square lattice is initially randomly filled with particles with a probability c, and in the following step new particles are adsorbed or existing particles desorbed according to the prescribed rules. This can be done either sequentially or parallelly. By "sequential" we mean that sites are scanned one after the other, and the adsorption or desorption is implemented for each site right away. "Parallel" means that the sites are scanned, and the required changes to be made are noted, without execution. Finally, after all sites are scanned, the neccessary changes are implemented simultaneously for all sites. The results may not agree in the two cases. We choose the parallel updating algorithm for the present study, as it is closer to reality in this case.

In the mobile case, the adsorbed molecules can move laterally on the surface. The physical situation simulated is described by Eq. (6). A two-dimensional square lattice of unit spacing and size 300×300 is occupied randomly with an initial coverage $c_{initial}$. Every occupied site is assigned the value 1, and empty sites are assigned the value 0. The occupied sites then desorb with a probability [according to Eq. (11)] which is the same for each occupied site,

$$f_e = \exp(-1/T^*).$$

For very large T^* the desorption probability approaches 1. The vacant sites are filled with a probability dependent on the number of occupied near neighbor sites n as f_c^n. After one round of adsorption and desorption is complete, the concentration of the occupied sites c_{final} is calculated. Periodic boundary conditions are used here.

In the next time step, the c_{final} of the previous time step becomes the new $c_{initial}$. The square lattice is then randomly occupied afresh with this $c_{initial}$. A complete time step begins with the random occupation of all sites with a $c_{initial}$ and ends with the assignment of c_{final} to the $c_{initial}$ of the next time step. This constitutes a feedback loop, similar to what is found in chemical systems showing oscillation. This iterative process stops when c_{final} saturates with increasing time to a definite value. In the simulation, we checked up to 50 000 time steps. The "mobility" of the molecules is simulated by the randomization of the concentration $c_{initial}$ in the beginning of every time step.

B. Immobile surface layer

If we consider the energy barrier to surface movement of the particles to be large enough, the arguments presented in the last subsection are not valid. We start with a certain concentration of particles randomly distributed on a square lattice and allow absorption and desorption according to our rules. But after one time step the distribution is no longer random, so we cannot find out the number of new adsorbed or desorbed sites as in Eq. (6). We can, however, simulate the system as above without the randomization procedure following each round of adsorption and desorption. This mimics the development of a surface layer where the particles are not free to move laterally on the surface. The results in this case are quite different.

III. RESULTS

We present the results for the mobile and immobile layer case. The mobile layer results are done analytically or by numerical iteration and verified by computer simulation. The immobile layer results are done by computer simulation as an analytical solution cannot be obtained here.

A. Results for the mobile layer

Figure 1(a) shows the bifurcation of the stable fixed point. The final coverage is plotted against $\exp(-1/T^*)$ for different pressures $P^* = 0.0$, 0.3, 0.6, and 0.9. The isobars have one steady-state solution up to a temperature T^*_b. At T^*_b the steady-state solution becomes unstable and two new solutions appear. This is the bifurcation point. Above T^*_b the system oscillates between these two states with different coverage. This can be demonstrated by substituting any of these coverages as c_i in Eqs. (12) and (13). Figure 1(b) shows how the temperature and coverage at the bifurcation point T^*_b and c_b vary with reduced pressure P^*. Above the bifurcation point, the system converges to a steady oscillation between the two solutions, from any starting point. Figures 2(a) and 2(b) show the typical cluster formations just at the bifurcation point for $P^* = 0.001$ and $T^*_b = 0.92$. This is a typical two-point limit cycle. These results are independent of the initial coverage.

For T^* very large and $P^* = 1$ there is an oscillation between $c_{initial}$ and $1 - c_{initial}$, as is also evident from Eq. (6).

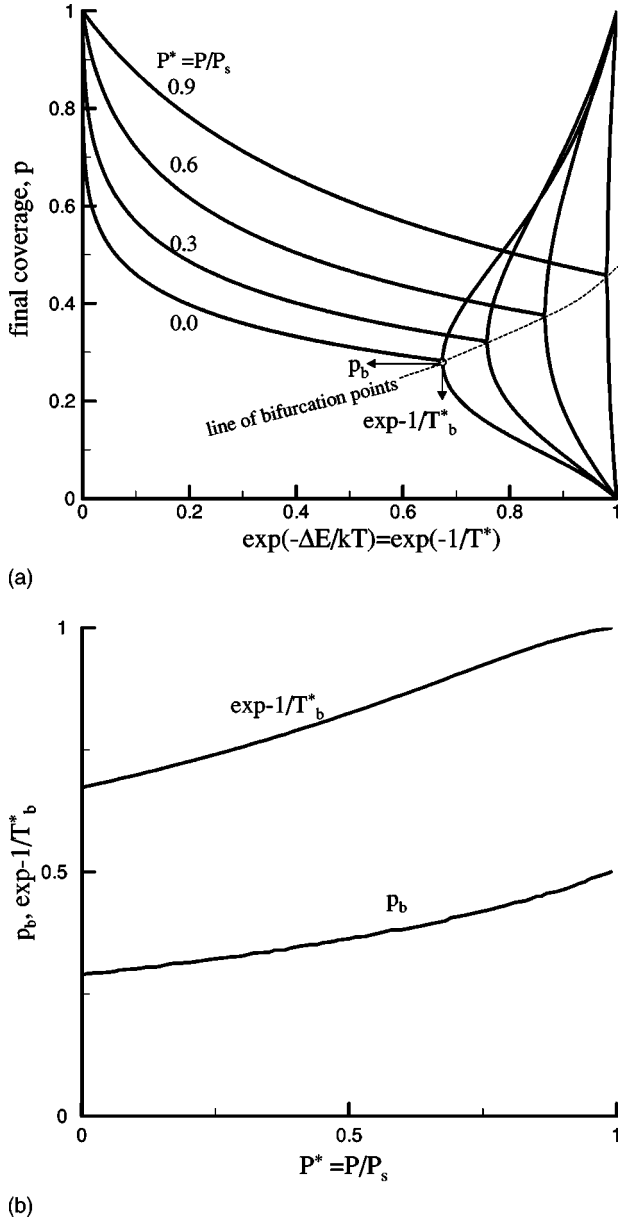

FIG. 1. (a) Isobars for the final coverage for the mobile layer. At T^*_b, the steady solution for c_b shows the bifurcation to a limit cycle. (b) Variation of T^*_b and c_b with P^*. Please refer to the text Sec. III A for a detailed discussion.

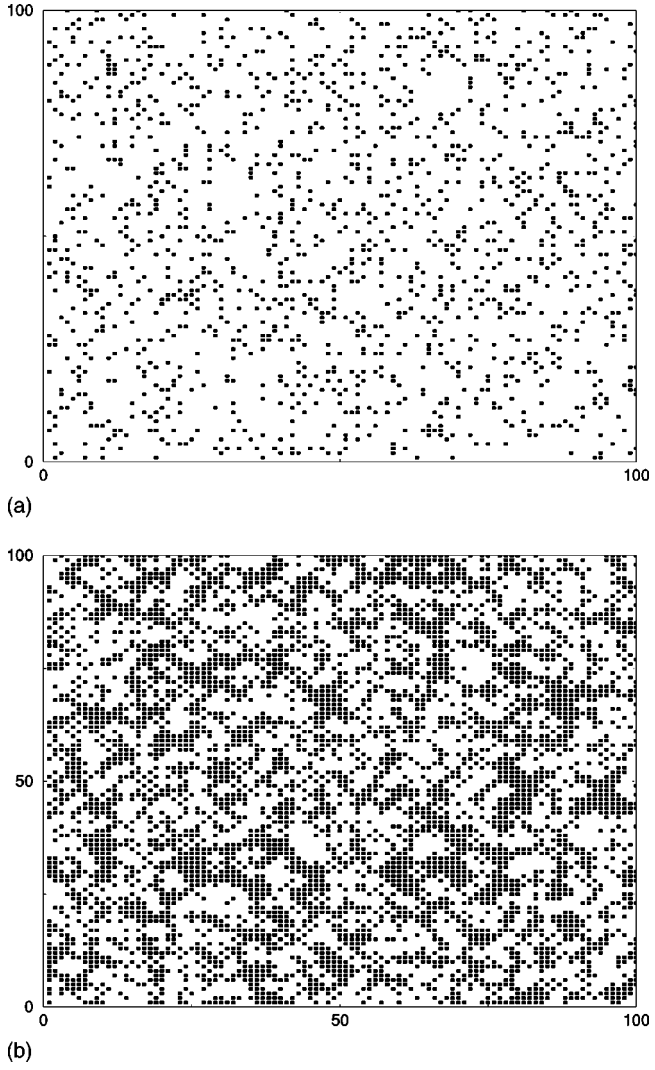

FIG. 2. (a) Typical cluster formation at $P^*=0.001$ and $T^*_b=0.92$, corresponding to the lower fixed coverage $c=0.144$ of the two-point limit cycle. (b) Typical cluster formation at $P^*=0.001$ and $T^*_b=0.92$, corresponding to the upper fixed coverage $c=0.491$ of the two-point limit cycle.

Here T^* always refers to the substrate temperature.

Systems governed by nonlinear equations do often exhibit such behavior [18], but we have not come across such a case in the adsorption problem, except the work of Patrylak *et al.* [12] where no explanation for the oscillation is offered. The results were checked for finite size effects on a 500×500 square lattice. The saturation values of coverage at different temperatures and pressure remained unchanged.

B. Results for the immobile surface layer

The immobile situation can be studied only by computer simulation. Starting with an initial random distribution of particles, the system is allowed to evolve and the final coverage for different P^* and T^* is studied. In this case as there is no randomization, the system takes a very long time to reach the steady state, and we have observed up to 30 000 time steps. Steady state solutions of c_{final} are obtained for $T^*<1$, i.e., $\Pi_{desorb}<1$. In the computer simulation for the immobile case, we find it convenient to use an effective temperature T_{sim} which takes values from 0 to 1 only. The desorption probability should be maximum, i.e., 1 at $T_{sim}=1$. So we define T_{sim} as

$$\Pi_{desorb} = e\,\exp(-T_{sim}) = \exp(1/T^*). \tag{14}$$

Figure 3 shows the coverage plotted against $\exp(-1/T_{sim})$, i.e., $[e\,\exp(-1/T^*)]$. Oscillations are obtained for $T^*=1$. No bifurcation is seen in Fig. 3 where the range for T^* is from 0 to 0.9. We have checked for T^* values up to 0.99 and have obtained no bifurcation. The steady state isobars and isotherms are shown in Figs. 3 and 4, respectively. In both these

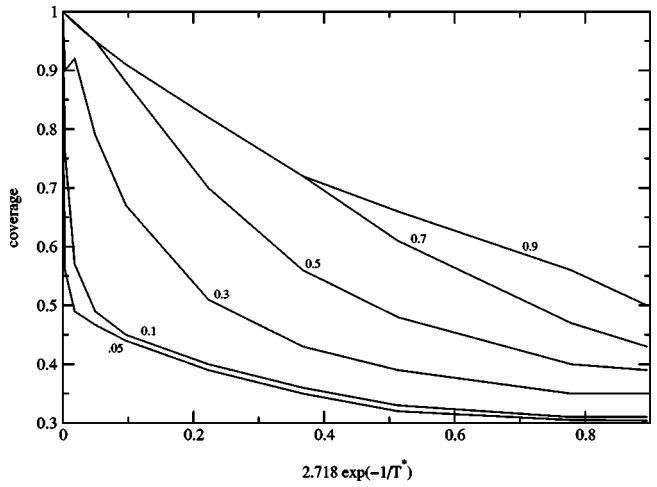

FIG. 3. Isobars for the immobile case showing variation of coverage with $2.718\exp(-1/T^*)$. The values of P^* for each curve are shown in the figure. Stable c are obtained for $2.718\exp(-1/T^*)$ up to 0.9, for $2.718\exp(-1/T^*)=1.0$ oscillations are obtained.

figures values of T^* only up to 0.9 are shown to avoid cluttering.

At $\Pi_{desorb}=1.0$, oscillations between a two-point limit sets in for all values P^*. For $P^*\leqslant 0.7$, the limit points of the two-point cycle are 0 and 1. As P^* increases to 0.9, the extremities of the limit cycle converge slightly to the values 0.11 and 0.89. However, for every P^*, there is a certain initial coverage c_α that yields a final coverage oscillating in a narrower confine between 0.4 and 0.5 for all P^*. Even a departure of 0.05 from c_α, shifts the final coverage to the fixed point limits of the wider limit cycle. However, the rate of convergence to c_{final} from different $c_{initial}$S other than c_α, is slower for higher values of P^*. The c_α increases slowly with P^* as displayed in Table I. Here too the results were checked for finite size effects. The limits for the oscillating coverage remained unchanged for the different combinations of pressure and temperature.

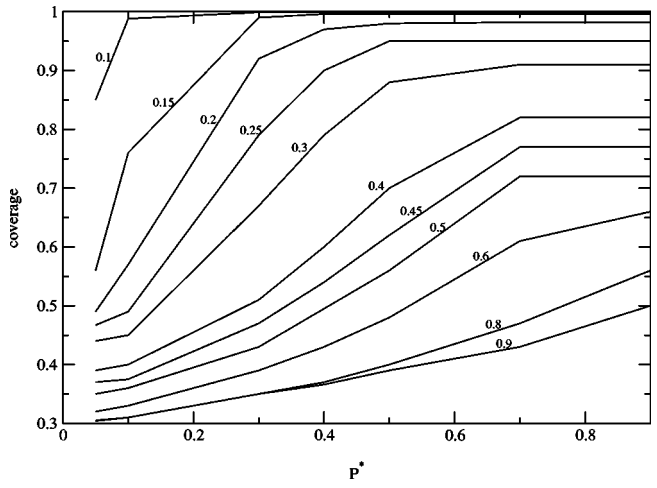

FIG. 4. Isotherms for the immobile case showing variation of coverage with pressure P^*. Stable c are obtained for $2.718\times\exp(-1/T^*)$ up to 0.9, for $2.718\exp(-1/T^*)=1.0$ oscillations are obtained.

TABLE I. The variation of c_α with P^*.

P^*	0.1	0.2	0.3	0.5	0.6	0.7	0.8	0.9
c_α	0.23	0.25	0.265	0.305	0.33	0.35	0.39	0.43

IV. DISCUSSION

We have demonstrated that the adsorption/desorption problem developed on a square lattice shows very interesting possibilities. The treatment here is similar to modifications of the percolation problem as in Manna *et al.* [6]. An initial random distribution of particles is allowed to evolve according to a prescribed set of rules. However, in the present work we are interested in how the coverage develops, as a function of time, rather than the percolation properties of the adsorbed layer.

Our approach differs from the usual treatment of the adsorption/desorption problem in chemical physics [15] in that we specify explicitly whether the adsorbed layer is mobile or immobile. From our point of view equating the adsorption and desorption probabilities to find the steady state coverage is valid only when the particles can rearrange very fast to preserve the random distribution. We demonstrate that making the particles truly immobile on the two-dimensional surface gives a quite different final coverage, which is also dependent on the initial coverage. This was discussed in the previous work [5] with an attractive interaction between particles. Careful experiments are needed to test the justification of these arguments. In our earlier work [5] we started with a randomly occupied square lattice and let particles desorb with a probability which decreased with the number of occupied neighboring sites. This amounted to an attractive interaction between the particles. The adsorption was a function of the pressure only. The most striking result of the present work is the observation of oscillations in the adsorption/desorption problem, using such an extremely simple model, without taking any details of the system into account.

Earlier well known works on nonlinear mathematical equations [18] show the appearance of bifurcations with repeated period doubling sometimes leading to chaos. Such situations are found in real life in problems of physics, chemistry, and biology. A nonequilibrium situation arising from a steadily maintained temperature difference leads to Benard convection [18]. Chemical systems are known to exhibit oscillations in concentration of reactants and products in chemical reactions under nonequilibrium conditions [19,20]. There is also some study of such a phenomenon in adsorption/desorption problems [12,10]. Experiments with repelling particles adsorbing on a substrate are reported in Ref. [11], but in this experiment two different types of particles are involved.

So in conclusion the simple stochastic model with adsorption and desorption on a square lattice gives rise to a host of interesting phenomena. With an attractive interaction between particles phase transitions and hysteresis was observed [5], while a repulsive interaction gives oscillations in coverage under certain conditions.

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